

English version

**Child use and care articles - Drinking equipment - Part 2:
Chemical requirements and tests**

Articles de puériculture - Articles pour l'alimentation liquide
- Partie 2: Exigences chimiques et essais

Artikel für Säuglinge und Kleinkinder - Artikel für flüssige
Kindernahrung - Teil 2: Chemische Anforderungen und
Prüfungen

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Foreword

This document (EN 14350-2:2004) has been prepared by Technical Committee CEN/TC 252 "Child use and care articles", the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2005, and conflicting national standards shall be withdrawn at the latest by February 2005.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

This European Standard EN 14350 "Child use and care articles – Drinking equipment" consists of the following parts:

- *Part 1: General and mechanical requirements and tests*
- *Part 2: Chemical requirements and tests*

Introduction

This document establishes minimum safety requirements and gives appropriate test methods for children's drinking equipment.

The complete document harmonises, for the first time, minimum safety requirements and test methods for children's drinking equipment. Some of the provisions have been taken from other existing national and European Standards and for these provisions the Technical Committee has relied on previous validation.

It is not permitted to claim compliance with individual parts of this document. Any claim relates to all published parts.

The use of this document may involve hazardous materials, operations and/or equipment. This document does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to its use.

It is recommended that manufacturers and suppliers operate to EN ISO 9001 [7] standard for quality management systems.

Elastomeric and rubber teats are regulated by the Commission Directive 93/11/EEC [1] concerning the release of *N*-Nitrosamine and *N*-Nitrosatable substances from elastomer or rubber teats and soothers. The current Directive provides in its annexes an outline method of analysis that has been published as EN 12868.

A limit for the release of 2-mercaptobenzothiazole (MBT) has been specified in the standard. This limit significantly reduces the level of this substance potentially released from children's drinking equipment. The Scientific Committee for Food has concluded that the limit does not constitute a health hazard. The limit for release of MBT will be reconsidered in light of future studies and recommendations.

A limit for the release of 2,2-bis(4-hydroxyphenyl)propane [Bisphenol A] (BPA) has been specified in the standard. The Scientific Committee for Food has concluded that the (temporary) limit (t-TDI) does not constitute a health hazard. The limit for release of BPA will be reconsidered in light of future studies and recommendations.

It is noted that all plastics components of drinking equipment are regulated by the Commission Directive 2002/72/EC [2] relating to plastics materials and articles intended to come into contact with foodstuff.

Commission Decision 99/815/EC [3], with its subsequent extensions, has adopted (temporary) measures prohibiting the placing on the market of toys and childcare articles intended to be placed in the mouth by children under three years of age. The prohibition relates to such products made of soft PVC containing one or more of the substances di-iso-nonyl phthalate (DINP), di-(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), di-iso-decyl phthalate (DIDP), di-n-octyl phthalate (DNOP) and butylbenzyl phthalate (BBP). At the time of preparing this document a final decision was awaited. This document will be reviewed in the light of that decision.

The Technical Committee has considered the issues relating to phthalate plasticiser migration from child use and care articles not intended to be placed in the mouth. Recognising the inadequacies of the only currently validated (static) test method for plasticiser migration from PVC [8], the Committee has developed an improved test to provide migration data under more realistic (dynamic) conditions of exposure. However, the Technical Committee will consider the official European method prior to its application to drinking equipment; such child use and care articles may require additional or alternative measures due to the mode of usage of drinking equipment and their potentially longer periods of exposure to babies and young children. After this consideration, an amendment to this document may be made.

Formaldehyde, caprolactam and colorants have each been considered by the Technical Committee. They have not been included in the document at this stage because of the lack of either adequate information for making a

satisfactory potential risk assessment, or validated test methods for the determination of their migration levels from relevant products. They will be reconsidered when further information becomes available.

For similar reasons, latex protein allergy risk has also not been included in this document. There is an extremely low incidence of latex protein allergy amongst babies and young children. Nevertheless, provision for information for drinking equipment containing natural rubber latex has been made in Part 1 of this document. The issue of potential sensitisation and allergic reaction from rubber products will be reconsidered when further information becomes available.

1 Scope

This part of this document specifies limits for the release of certain chemicals from materials to be used for the manufacture of the following drinking equipment:

- Re-usable feeding teats and drinking accessories;
- Re-usable feeding bottles and drinking cups;
- Single-use feeding bottles, feeding teats, feeding bags and drinking accessories, which do not contain fluid when purchased.

It includes test methods for the chemical safety requirements specified.

It does not apply to drinking equipment designed for medical applications or for use under medical supervision.

This document is not applicable to soothers. Safety requirements and test methods for soothers are specified in EN 1400-1, EN 1400-2 and EN 1400-3.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 71-3, *Safety of toys – Part 3: Migration of certain elements*.

EN 12868, *Child use and care articles - Methods for determining the release of N-Nitrosamines and N-Nitrosatable substances from elastomer or rubber teats and soothers*.

EN ISO 3696, *Water for analytical laboratory use – Specification and test methods (ISO 3696:1987)*.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

feeding teat

substitute mother's nipple that when attached to a container permits a child to obtain fluid by suckling

3.2

drinking accessory

any device other than a feeding teat which permits a child to obtain fluid from a container

EXAMPLE feeding spout.

3.2.1

straw

hollow tube drinking accessory through which fluid is sucked

3.3

container

either a feeding bottle, drinking cup or feeding bag

3.3.1

feeding bottle

container which is capable of holding a fluid and incorporates a graduated scale suitable for visual measurement and is intended for feeding a child through a feeding teat or drinking accessory

3.3.2

drinking cup

container other than a feeding bottle or feeding bag capable of holding a fluid intended for feeding a child

3.3.3

feeding bag

bag capable of holding fluid and supported for use by a holder

NOTE Feeding bags are also known as feeding liners.

3.4

locking ring

component used to secure a feeding teat or drinking accessory to a container

3.5

sealing disc

component used to create a seal between the container and the locking ring

3.6

protective cover

component to cover a feeding teat or drinking accessory

3.7

matched components

any of the above defined components which are used together whilst feeding a child

3.8

numbered graduations

numbered markings which indicate the volume of fluid within the container

3.9

single-use feeding teat, drinking accessory or container

any item of drinking equipment sold for single use

3.10

re-usable

component intended to be used again after first use

3.11

protrusions

drinking accessory, feeding teat or spoon, excluding straws

4 Requirements

4.1 General

Materials used for the manufacture of drinking equipment shall be subjected to the tests listed in Table 1 and shall conform to 4.4 to 4.9.

NOTE 1 Additional information for the finished product can be obtained from Directives 82/711/EEC [4] and amendments 93/8/EEC and 97/48/EC, 85/572/EEC [5], 89/109/EEC [6], and 2002/72/EC [2].

NOTE 2 It is recommended that manufacturers and suppliers operate to EN ISO 9001 for quality management systems.

4.2 Chemical properties

The vulcanising agents (MBT), antioxidants, and Bisphenol A (BPA) do not represent a definitive list. Chemicals other than those mentioned in this document may be used where toxicological evidence, either on the original chemical or any reaction product, is available to demonstrate that no unacceptable risk will be posed when they are used in drinking equipment and an appropriate analytical test procedure for determining migration levels exists.

4.3 Requirements by material

Materials used in the manufacture of components of drinking equipment shall be subjected to the tests marked with an x in Table 1.

Table 1 — Tests to be carried out on materials

Material						
	Migration of certain elements (see 5.2)	<i>N</i> -Nitrosamines and <i>N</i> -Nitrosatables release (see 5.3)	MBT release (see 5.4)	Anti-oxidants release (see 5.4)	BPA release (see 5.5)	Volatile compounds content (see 5.6)
Vulcanised rubber	x	x	x	x		
Silicone rubber	x	x				x
Thermoplastic elastomers (TPEs)	x	x				
Glass	x					
Thermoplastics	x				x ^a	
^a Only thermoplastics containing polycarbonate or polysulfone shall be tested for Bisphenol A release						

4.4 Migration of certain elements

When tested in accordance with 5.2 the migration of elements from all material(s) used in the manufacture of drinking equipment shall not exceed the limits given in Table 2.

When drinking equipment contain components manufactured from different material(s), or in different colours, all components shall be tested individually. Decorations shall be considered to be part(s) of the material(s) on which they are printed.

Table 2 — Limits of element migration from drinking equipment

Element	Limit (mg/kg)
Antimony, Sb	15
Arsenic, As	10
Barium, Ba	100
Cadmium, Cd	20
Lead, Pb	25
Chromium, Cr	10
Mercury, Hg	10
Selenium, Se	100

NOTE The analytical method specified in EN 71-3 has been applied in this document to drinking equipment. The limits have been set based on the limit of detection for each element using commonly available analytical techniques.

4.5 *N*-Nitrosamines and *N*-Nitrosatables release

When tested in accordance with 5.3, the total *N*-Nitrosamines and *N*-Nitrosatables release of any elastomer or rubber component shall not exceed the limits given in Table 3.

Table 3 — *N*-Nitrosamines and *N*-Nitrosatables release and tolerances

Substance	Limit mg/kg	Tolerance mg/kg
<i>N</i> -Nitrosamines	0,01	0,01
<i>N</i> -Nitrosatables	0,1	0,1

4.6 2-mercaptobenzothiazole (MBT) release

When elastomeric components of drinking equipment are tested according to 5.4, the migration of the following chemical shall not exceed 8 mg/kg:

2-mercaptobenzothiazole or 2(3H)-benzothiazolethione

CAS No. 149-30-4

IUPAC 1,3-benzothiazole-2-thiol

4.7 Antioxidants release

When elastomeric components of drinking equipment are tested according to 5.4, the migration of the following chemical shall not exceed 30 µg/100 ml or 60 µg/dm²:

2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (BHT)

CAS No. 128-37-0

IUPAC 2,6-di-tert-butyl-*p*-cresol

When elastomeric components of drinking equipment are tested according to 5.4, the migration of the following chemical shall not exceed 15 µg/100 ml or 30 µg/dm²:

2,2'-methylenebis(6-(1,1-dimethylethyl)-4-methyl-phenol) (Antioxidant 2246)

CAS No. 119-47-1

IUPAC 6,6'-di-tert-butyl-2,2'-methylenedi-*p*-cresol

4.8 2,2-bis(4-hydroxyphenyl)propane [Bisphenol A] (BPA) release

When thermoplastic components of drinking equipment are tested according to 5.5, the migration of the following chemical shall not exceed 0,03 µg/ml:

2,2-bis(4-hydroxyphenyl)propane [Bisphenol A] (BPA)

CAS No. 80-05-7

IUPAC 4,4'-(methylethylidene)-bisphenol or 4,4'-isopropylidenediphenol

4.9 Volatile compounds content

When silicone rubber components of drinking equipment are tested according to 5.6, the volatile compounds content shall not exceed 0,5 % (m/m).

5 Test methods

5.1 Sample preparation

The sample preparation applies to all tests excepting 5.3.

5.1.1 Samples from re-usable products shall be immersed in boiling water (conforming to EN ISO 3696 Grade 3) for 10 min without touching the walls of the container.

NOTE This is to remove the surface coating arising from the manufacturing processes and ensure that the materials used are stable in boiling water.

5.1.2 New samples, preferably from the same batch, shall be used for each test.

5.1.3 Samples and test portions shall only be handled with suitable (non-rubber or plastic) gloves and shall only be stored in securely fastened, migration-free (glass) containers and protected from light.

5.2 Determination of the migration of certain elements

5.2.1 Principle

The analytical method specified in EN 71-3 has been applied in this document to drinking equipment. Soluble elements (antimony, arsenic, barium, cadmium, chromium, lead, mercury and selenium) are extracted from the individual components of the drinking equipment that are accessible to the child. Conditions that simulate contact with stomach acid shall be used. The concentrations of the soluble elements are described quantitatively.

5.2.2 Apparatus

5.2.2.1 Water bath, able to maintain the temperature of the test mixture at $(37 \pm 2) ^\circ\text{C}$ and having the means to agitate the test mixture.

5.2.2.2 pH meter, with an accuracy of $\pm 0,2$ pH units.

5.2.2.3 Membrane filter with a pore size of 0,45 µm.

5.2.2.4 Centrifuge capable of centrifuging at $(5\,000 \pm 500)$ rpm.

5.2.3 Reagents (analytical reagent grade unless otherwise specified)

5.2.3.1 Hydrochloric acid solution, $(0,07 \pm 0,005)$ mol/l.

5.2.3.2 Hydrochloric acid solution, $(2,0 \pm 0,2)$ mol/l.

5.2.3.3 Distilled water.

5.2.4 Selection of test portions

Test portions shall be taken from each individual component of the drinking equipment that is accessible to the child. Components that are joined together shall be separated and tested as separate items.

5.2.5 Preparation of test portion

At least 100 mg, and preferably at least 1 g, of a representative test portion of each individual component of the drinking equipment shall be obtained. Heating of the materials, whilst separating components and during cutting into pieces, shall be avoided.

Feeding teats shall be cut length-wise only once. All other components shall be cut, as far as is possible, into pieces of length 4 mm to 6 mm and width not exceeding 6 mm.

5.2.6 Procedure

Mix, at (37 ± 2) °C, the prepared test portion (see 5.2.5) with 50 times its mass of an aqueous solution of the hydrochloric acid (5.2.3.1) in a container of 1,5 to 5 times the volume of acid. Agitate the container in the water bath (5.2.2.1) for (60 ± 5) s and determine the acidity of the mixture with the pH meter (5.2.2.2). If the pH is $> 1,5$, add drop-wise, whilst continuing to shake the mixture, an aqueous solution of hydrochloric acid (5.2.3.2) until the pH is in the range of 1,0 to 1,5. The mixture shall be protected from light and continuously agitated under similar conditions for a further (60 ± 1) min before being allowed to stand for (60 ± 1) min at the same temperature.

Immediately after standing, separate the solids from the solution by membrane filtration (5.2.2.3) and, if necessary, centrifugation (5.2.2.4) at up to 5 000 r/min and for no longer than 10 min. The use of centrifugation shall be reported.

If the solutions are to be kept for more than 1 d prior to analysis, they shall be stabilised by the addition of hydrochloric acid so that the concentration of the stored solution is approximately 1 mol/l.

5.2.7 Determination of the quantity of migrated elements

Methods having a detection limit of at least 0,1 times the values of the elements to be measured shall be used to determine their quantity.

NOTE The detection limit of a method is deemed to be 3 times the standard deviation of the blank value measured by the laboratory carrying out the analysis.

5.3 Determination of *N*-Nitrosamines and *N*-Nitrosatables release

The levels of *N*-Nitrosamines and *N*-Nitrosatable substances present in the drinking equipment shall be determined using the method detailed in EN 12868.

5.4 Determination of 2-mercaptobenzothiazole (MBT) and antioxidants release

5.4.1 Principle

MBT and its metal-salts are determined quantitatively following extraction into aqueous migration liquids. MBT is identified and determined by High Performance Liquid Chromatography (HPLC) and ultra violet (UV) detection at a specific wavelength, either by direct injection of the aqueous migration liquid, or in a concentrated solution. The identification is confirmed by comparing the UV-spectrum of the sample peak produced by a diode array detector with the spectrum of the peak of an authentic MBT-sample.

NOTE The method is based on the published work of G.Blosczyk and H.-J.Domling [9] and G.Blosczyk [10].

The method is also used for the qualitative and quantitative determination of the antioxidants 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (Antioxidant BHT) and 2,2'-methylenebis(6-(1,1-dimethylethyl)-4-methyl-phenol) (Antioxidant 2246). They too are identified and determined by HPLC and UV-detection at a specific wavelength. The identification is confirmed by comparing the UV-spectra of the sample peaks produced by a diode array detector with the spectra of the peaks of authentic substances. For unknown samples a further identification step by thin layer chromatography (TLC) or gas liquid chromatography (GLC) is recommended.

5.4.2 Apparatus

5.4.2.1 HPLC with a 20 µl injection loop diode array detector connected to an integrator or personal computer with chromatography software.

5.4.2.2 HPLC-column capable of separating MBT from the antioxidants and fully resolving the antioxidants such that the peaks do not overlap by more than 1 % peak area with each other and with interferences arising from other sample ingredients.

5.4.3 Reagents: Chemicals (analytical reagent grade unless otherwise specified)

5.4.3.1 Water (HPLC grade).

5.4.3.2 Acetonitrile (HPLC grade).

5.4.3.3 Distilled water.

5.4.3.4 Dichloromethane (Residue analysis grade).

5.4.3.5 Anhydrous sodium sulphate.

5.4.3.6 Acetic acid, 3 % (w/v) aqueous solution.

5.4.4 Reagents: authentic samples (purity greater than 98 %)

5.4.4.1 2-mercaptobenzothiazole (MBT).

5.4.4.2 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (Antioxidant BHT).

5.4.4.3 2,2'-methylenebis(6-(1,1-dimethylethyl)-4-methyl-phenol) (Antioxidant 2246).

5.4.5 Reagents: standard solutions

5.4.5.1 Standard MBT solution.

Prepare six standard solutions containing for example 1,0 mg, 2,0 mg, 5,0 mg, 10,0 mg, 15,0 mg and 20,0 mg MBT (5.4.4.1)/l of acetonitrile (5.4.3.2).

5.4.5.2 Standard antioxidants solution.

Prepare a solution of the two antioxidants containing 30 µg Antioxidant BHT (5.4.4.2) and 15 µg of Antioxidant 2246 (5.4.4.3) in 5 ml of acetonitrile (5.4.3.2).

5.4.6 Procedure

Weigh 1 dm² or, if 1 dm² is not available, the largest possible area of the pre-treated sample and cut it into as few parts as possible. The number of parts shall be defined by the size of the neck of a 250 ml flask. The area of the sample shall be the sum of the areas of the inner and outer surfaces.

NOTE 1 Cutting into two pieces is usually sufficient for a feeding test.

NOTE 2 To aid measurement of area, cut the elastomeric or thermoplastic part into several pieces and draw around them on millimetre paper. Count the number of squares within each line and add the number together.

Store the sample for 24 h in the aqueous migration liquids (water to represent milk and 3 % acetic acid to represent fruit juices) at 40 °C in a drying oven in the ratio of 1 cm²/2 ml aqueous migration liquid.

After removing the solid parts, shake the aqueous migration liquid with two 50 ml aliquots of dichloromethane (5.4.3.4). The combined organic phases are dried over anhydrous sodium sulphate (5.4.3.5) and evaporated carefully to dryness. The residue is then re-dissolved in 5 ml of acetonitrile (5.4.3.2).

NOTE Concentration columns may be used to replace shaking with dichloromethane.

5.4.7 Calculation

5.4.7.1 MBT

Inject the six standard solutions (5.4.5.1) into a HPLC (5.4.2.1) with HPLC column (5.4.2.2) three times each. Produce a calibration curve of mg MBT/kg material using the eighteen values.

Inject the test solution (5.4.6) into the HPLC. Use the calibration curve to determine the MBT-content of the test solution, either manually or with data-handling software. A detection limit of ≤ 0,1 µg MBT/ml sample solution shall be obtained.

NOTE 1 A suitable HPLC apparatus, method and precision data are described in Annex A.

NOTE 2 The calibration curve should be rectilinear and the correlation coefficient 0,997 or better.

NOTE 3 It is recommended that the test be carried out at least in duplicate.

5.4.7.2 Antioxidants

Inject the standard solution (5.4.5.2) into a HPLC (5.4.2.1) with HPLC column (5.4.2.2). Inject the sample solution (5.4.6) in the same way. Determine the amounts of migrated antioxidants, in mg antioxidant/cm² material, by comparison of the peak areas in the chromatograms of the standard solution and the sample solution, either manually or with data handling software.

If the peak areas of the antioxidants in the test solution are greater than the standard peak areas, prepare and obtain chromatograms of additional standard solutions in order to create a calibration curve over the region of interest. Obtain the amounts of migrated antioxidants from the calibration curve.

NOTE 1 A suitable HPLC apparatus, method and precision data are described in Annex A.

NOTE 2 It is recommended that the test be carried out at least in duplicate.

5.5 Determination of 2,2-bis(4-hydroxyphenyl)propane [Bisphenol A] (BPA) release

5.5.1 Principle

BPA is extracted from the test articles into aqueous food simulants, identified and its level determined by high performance liquid chromatography (HPLC) with fluorescence detection (FLD)¹⁾.

NOTE 1 Only FLD is applicable for concentrations of BPA below 0,1 µg/ml.

NOTE 2 Alternative methodology, such as gas chromatography (GC), has been documented and may be used. However, in comparison with the gas chromatographic method, the HPLC method has the advantage that BPA can be determined directly in the migrate without pre-concentration and derivatisation.

5.5.2 Apparatus

5.5.2.1 HPLC, preferably equipped with an automatic 50 µl loop injector and a fluorescence detector and data-handling software.

5.5.2.2 HPLC column capable of separating BPA fully from peaks originating from simulants and/or solvents used.

5.5.2.3 Membrane filter with a pore size of 0,45 µm.

5.5.2.4 Analytical balance with sensitivity of 0,0001 g.

5.5.2.5 Micro syringes: 10 µl, 20 µl and 50 µl.

5.5.3 Reagents: chemicals (analytical reagent grade unless otherwise specified)

5.5.3.1 Water (HPLC grade).

5.5.3.2 Methanol (HPLC grade).

5.5.3.3 Distilled water.

5.5.3.4 Acetic acid, 3 % (w/v) aqueous solution.

5.5.4 Reagents: authentic samples (purity greater than 98 %)

5.5.4.1 2,2-bis(4-hydroxyphenyl)propane [Bisphenol A] (BPA).

5.5.5 Reagents: standard solutions

5.5.5.1 Stock standard solution of BPA in methanol at defined concentration of approx. 1,0 mg/ml.

Weigh to the nearest 0,1 mg approx. 100 mg BPA (5.5.4.1) into a 100 ml volumetric flask. Dissolve the BPA in methanol (5.5.3.2) and make up to the mark with methanol.

Calculate the concentration in µg BPA/ml solution.

Repeat the procedure to obtain a second stock solution.

NOTE The solution may be stored refrigerated at +4 °C in a closed container, free from light for a period of at least 3 weeks.

1) This method is partially based on prCEN/TS 13130-13 [11]

5.5.5.2 Calibration solution

Transfer by micro syringe 0 µl, 10,0 µl, 20,0 µl, 30,0 µl, 40,0 µl, 50,0 µl of the stock standard solution (5.5.5.1) into a series of six 1 000 ml volumetric flasks and make up to the mark with fresh analyte-free aqueous food simulant (5.5.3.3 or 5.5.3.4) and mix thoroughly.

Repeat the procedure with the other analyte-free aqueous food simulant (5.5.3.3 or 5.5.3.4).

Calculate the exact concentrations of BPA in the calibration samples in µg/ml.

For at least one food simulant, repeat the procedure using the second stock solution (5.5.5.1).

5.5.6 Procedure

Transfer 100 ml of the aqueous food simulant (5.5.3.3 or 5.5.3.4) into the drinking equipment. If this volume is too large for the test article, then use a known volume equivalent to 50 % of the capacity of the drinking equipment. Store under static conditions for 24 h at 40 °C in a drying oven before transferring approx. 1 ml of the solution into a vial suitable for HPLC injection.

Repeat the procedure using the other aqueous food simulant (5.5.3.3 or 5.5.3.4).

If storage is necessary, sample solutions shall be refrigerated at +4 °C in closed containers, free from light.

5.5.7 Determination of the quantity of migrated BPA

Inject the calibration solutions (5.5.5.2) into a HPLC (5.5.2.1) with HPLC column (5.5.2.2). Produce calibration curves of µg BPA/ml food simulant using the twelve values for each stock solution.

NOTE The calibration curve should be rectilinear and the correlation coefficient 0,997 or better. The two sets of calibration solutions made from independently prepared stock solutions should be cross-checked by generating two calibration curves which, on the basis of peak ratio measurement, should agree to ± 5 % of one another.

Inject the test sample solutions (5.5.6) into the HPLC. Use the calibration curve to determine the BPA-content of the test solution, either manually or with data-handling software. A detection limit of ≤ 20 µg BPA/l sample solution (0,02 µg BPA/ml) shall be obtained.

NOTE 1 A suitable HPLC apparatus and method are described in Annex B.

NOTE 2 It is recommended that the test be carried out at least in duplicate.

5.6 Determination of volatile compounds content

5.6.1 Procedure

All weighings shall be with an accuracy of at least $\pm 0,1$ mg.

Drain excess water from the sample preparation stage (5.1.1).

Pre-heat an open, shallow container for 1 h at (100 ± 5) °C. Cool the container in a desiccator for 1 h and weigh (weight a).

Place approximately 10 g of the whole sample into the container and place in a drying oven at (100 ± 5) °C with fresh air inlet. After 1 h, cool the container and sample in a desiccator for at least 2 h and weigh (weight b).

Replace the container with the sample in a drying oven at (200 ± 5) °C with fresh air inlet. After 4 h, cool the container and sample in a desiccator for at least 2 h and re-weigh (weight c.)

The volatile compounds content is calculated from the percentage weight difference between weight b and weight c, after deducting the weight of the container (weight a).

NOTE It is recommended that the test be carried out at least in duplicate.

Annex A (informative)

Suitable HPLC apparatus, method and precision data for the determination of 2-mercaptobenzothiazole (MBT) and/or antioxidants

The following column has been found to be suitable: Reversed phase C₈, e.g. Spherisorb C₈, 5 µm diameter, length 25 cm.

The following operating conditions have been found to be suitable for this column: Mobile phase (Eluent A) : water containing 1 % acetonitrile, and Mobile phase (Eluent B) : acetonitrile. The mobile phase may require degassing.

The gradient programme is shown in Table A.1:

Table A.1 — Gradient programme

Time (min)	% Eluent A	% Eluent B
0 to 2	70	30
2 to 17 linearly to	10	90
17 to 22	10	90
22 to 25 linearly to	70	30
25 to 28 ^a	70	30
^a Or longer, if further equilibration is thought to be necessary		

The gradient of the eluent may need to be adjusted if a different column to that described above is used.

Flow rate: 1 ml/min.

Detection:

- a) MBT: UV 320 nm, Diode array spectrum from 240 nm to 360 nm, Detector programming from time 5 min to 12 min;
- b) Antioxidants: UV 280 nm, Diode array spectrum from 240 nm to 360 nm, Detector programming from time 12 min to time 25 min.

Retention times:

- a) MBT: approximately 9 min (max. 320 nm);
- b) Antioxidant BHT: approximately 20 min (max. 278 nm);
Antioxidant 2246: approximately 21 min (max. 282 nm).

Injection volume: 20 µl.

Depending on the type of equipment used, the appropriate operating conditions may need to be established.

Typical chromatograms for MBT and the antioxidants BHT and 2246 are shown in Figure A.1.

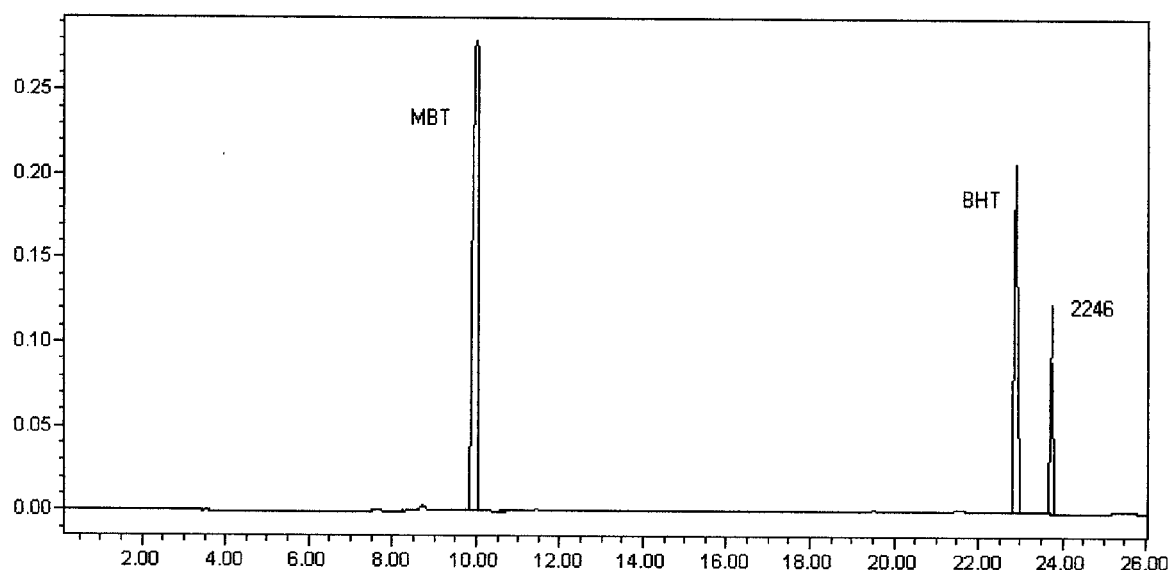


Figure A.1 – Chromatograms of MBT and antioxidants (absorbance (absorbance units) v. retention time (min))

Precision data

Statistical analysis of a recent collaborative trial undertaken by seven laboratories has shown the repeatability and reproducibility of the method for MBT to be:

average repeatability, $r = 3,0$; and

average reproducibility $R = 7,4$

and the coefficient of variation of the repeatability and reproducibility to be:

average coefficient of variation of repeatability $CV_r = 10,4 \%$; and

average coefficient of variation of reproducibility $CV_R = 23,4 \%$.

NOTE Coefficient variation CV is the ratio of the standard deviation to the average according to ISO 3534-1 [12].

Annex B (informative)

Suitable HPLC apparatus and method for the determination of 2,2-bis(4-hydroxyphenyl)propane [Bisphenol A] (BPA)

The following columns and operating conditions have been found to be suitable for the determination of BPA :

Column:	LATEK 250 mm x 4 mm Nucleosil 100-5-C18.
Column temperature:	25 °C.
Mobile phase:	Methanol : water (65 : 35); isocratic.
Flow:	0,6 ml/min.
Injection volume:	40 µl.
Detection:	BPA: FLD; excitation wavelength Ex = 275 nm, emission wavelength Em = 313 nm.
Retention time:	BPA; approximately 10,2 min.

Or

Column:	stainless steel 250 x 4,6 mm packed with C18-coated spherical silicagel, particle size 5 µm (load of 9 % carbon and end-capped) (Hypersil ODS 5 µm).
Column temperature:	25 °C.
Mobile phase:	Methanol : water (70 : 30).
Flow:	1,0 ml/min.
Injection volume:	40 µl.
Detection:	BPA: FLD; excitation wavelength Ex = 275 nm, emission wavelength Em = 313 nm.
Retention time:	BPA; approximately 4,5 min.

Depending on the type of equipment used, the appropriate operating conditions may need to be established.

A typical chromatogram for BPA is shown in Figure B.1.

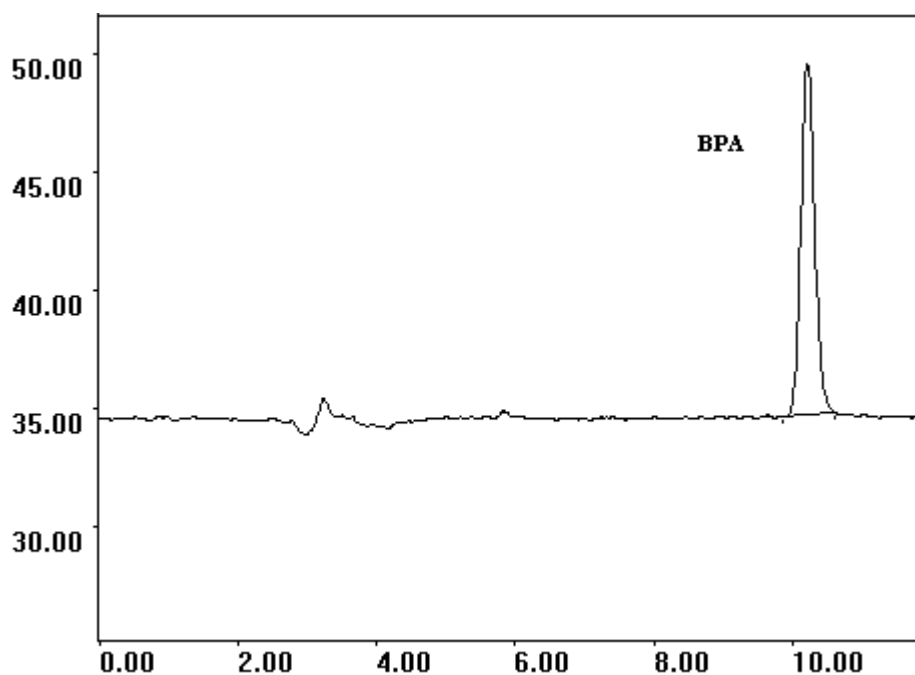


Figure B.1 – Chromatogram of BPA (absorbance (volt) v. retention time (min))

Precision data

This method has not been validated by collaborative trial. It has however been subject to a peer review procedure following method development work.

The within-laboratory relative standard deviation (RSD) of the method was found to be less than 4,5 % and typically less than 2,0 %.

Bibliography

This European Standard incorporates references to EU Directives and other publications. These references are cited at the appropriate place in the text and the publications list hereafter.

- | | |
|---|---|
| [1] Commission Directive 93/11/EEC | Commission Directive of 15 March 1993 concerning release of <i>N</i> -Nitrosamines and <i>N</i> -Nitrosatable substances from elastomer or rubber teats and soothers. |
| [2] Commission Directive 2002/72/EC | Commission Directive of 6 August 2002 relating to plastic materials and articles intended to come into contact with foodstuffs. |
| [3] Commission Decision 99/815/EC and subsequent extensions | Commission Decision of 7 December 1999 adopting measures prohibiting the placing on the market of toys and childcare articles intended to be placed in the mouth by children under three years of age made of soft PVC containing one or more of the substances di-iso-nonyl phthalate (DINP), di-(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), di-iso-decyl phthalate (DIDP), di-n-octyl phthalate (DNOP) and butylbenzyl phthalate (BBP). |
| [4] Commission Directive 82/711/EEC, and amendments 93/8/EEC and 97/48/EC | Commission Directive of 18 October 1982 laying down the basic rules necessary for testing migration of the constituents of plastic materials and articles intended to come into contact with foodstuffs. |
| [5] Council Directive 85/572/EEC | Council Directive of 19 December 1985 laying down the list of simulants to be used for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs. |
| [6] Council Directive 89/109/EEC | Council Directive of 21 December 1989 on the approximation of the laws of the Member States relating to materials and articles intended to come into contact with foodstuffs. |

Other publications

- [7] EN ISO 9001, *Quality management systems – Requirements (ISO 9001:2000)*.
- [8] CR 13387, *Child use and care articles - General and common safety guidelines*
- [9] G. Blosczyk and H.-J. Doemling, *Lebensmittelchemie und gerichtl. Chemie*, **36**, 90 (1982).
- [10] G. Blosczyk, *Deutsche Lebensmittel Rundschau*, **88**, 392 (1992).
- [11] prCEN/TS 13130-13, *Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 13: Determination of 2,2-bis(4-hydroxyphenyl) propane (Bisphenol A) in food simulants*.
- [12] ISO 3534-1, *Statistics - Vocabulary and symbols - Part 1: Probability and general statistical terms*.
- EN 1400-1, *Child use and care articles – Soothers for babies and young children – Part 1: General safety requirements and product information*.
- EN 1400-2, *Child use and care articles – Soothers for babies and young children – Part 2: Mechanical requirements and tests*.
- EN 1400-3, *Child use and care articles – Soothers for babies and young children - Part 3: Chemical requirements and tests*.